

Triglyceride Microemulsions: Effect of Nonionic Surfactants and the Nature of the Oil

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The phase behavior of mixtures of food grade surfactants and various triglycerides was investigated to prepare oil-in-water microemulsions (L_1) for food uses. Water-in-oil microemulsions (L_2) were easily formed at a ratio of 75/25 wt % ethoxylated monodiglycerides/monoglyceride. This ratio was found to be optimal for the formation of an extended triglyceride microemulsion area which approached the aqueous corner of the phase diagram where oil-in-water microemulsions (L_1) are present. Blue-phase regions, which are extremely stable emulsions, were identified. These regions consisted of droplets separated by layers of lamellar liquid crystals. Sucrose enhanced the formation of the L_1 phase while destroying the L_2 phase. Triglycerides containing unsaturated or short-chain fatty acids had improved solubility in L_1 -type microemulsions compared to triglycerides with saturated or long-chain fatty acids.

Microemulsions are thermodynamically stable suspensions usually containing two immiscible liquids, generally a hydrocarbon and an aqueous phase. Food formulations containing lipids and oils with limited solubility are in increasing demand for the preparation of low-fat products such as cream liqueurs, sauces, and salad dressings. Vegetable oils such as soybean and peanut oils contain long-chain fatty acids, mainly C_{16} and C_{18} , resulting in large triglyceride structures that are difficult to solubilize into microemulsions systems. As a result, liquid crystalline mesophases are often formed preferentially. However, a few microemulsion systems based on triglycerides have been reported in the literature (Dunn and Bagby, 1993; Friberg and Rydhag, 1971; Schwab et al., 1983; Hernqvist, 1986). Alander and Warenheim (1989a,b) have compared triglyceride behavior of microemulsions to that of ordinary hydrocarbons. They concluded that triglycerides, in particular long-chain fatty acid glycerides such as those of peanut oil, were considerably more difficult to solubilize into microemulsions than hydrocarbons or alkyl esters. Lindstrom et al. (1981) studied another system containing triglyceride, monoglyceride, and an aqueous phase and ultimately characterized small limited areas of water-in-oil microemulsions (L_2). Microemulsions of edible oils in a matrix of water and different hydrotropes which have been used as flavors or essential oil carriers have been reported in the patent literature (Wolf and Hauakotta, 1989; El-Nokaly et al., 1991). Dunn et al. (1992, 1993) have investigated the solubility of triglycerides in methanol solutions using mixed amphiphile systems containing long-chain fatty alcohols and medium-chain alkanols. They concluded that the formation of large aggregates resembling nonaqueous microemulsions was feasible under very limited conditions.

Recently, we have demonstrated (Joubran et al., 1993, 1994) that the formation of triglyceride microemulsions could be achieved by incorporating sucrose and short-chain alcohols such as ethanol. The alcohol acted synergistically with sucrose to destabilize the liquid crystalline mesophases, thus promoting the formation of triglyceride microemulsions which were confirmed by X-ray diffraction and polarized light microscopy.

This study was directed toward examining the effects on phase behavior and formation of microemulsions using

different vegetable oils, e.g., soybean oil and hydrogenated soybean oil, coconut oil, and fractionated coconut oil. Several ratios of food grade nonionic surfactants, ethoxylated monodiglycerides, and monoglyceride were used in conjunction with the hydrotropes, ethanol, propylene glycol, and sucrose. The principal objective of the research was to solubilize the triglycerides at lower temperatures so as to move the isotropic regions, prepared by using high surfactant concentrations, to areas of lower concentrations. Hydrotropes were studied to create a base for future studies to produce creams and sauces with high shelf-life stability and low fat content.

MATERIALS AND METHODS

Materials. The nonionic surfactant, ethoxylated monodiglycerides (Mazol 80 MGK, lot 95721), is a mixture of stearates and palmitate partial esters of glycerine condensed with approximately 20 mol of ethylene oxide/mol of α -monoglyceride reaction mixture (PPG Industries Inc., Gurnee, IL). Analysis indicated acid value = 2, saponification value = 65–75, hydroxyl value = 65–80, and iodine value (IV) = 2. The monoglyceride (Dimodan LSK, lot T-01136) was minimum 90% monoester and IV = 110 (Grindsted Products Inc., Industrial Airport, KS). Soybean oil, IV = 130, and hydrogenated soybean oil, IV = 76, were obtained from Central Soya Inc. (Fort Wayne, IN) and Adumim Chemical Ltd. (Israel), respectively. Coconut oil, IV = 11, melting point 25–27 °C, was from Stepan (lot 097740), and fractionated coconut oil mixture (Delios S), which contains 75% and 25% caprylic and capric acids, respectively, was from Henkel Corp. (Cincinnati, OH). Ethyl alcohol (200 proof) was purchased from Pharmco Ltd., and propylene glycol and sucrose were from Sigma (St. Louis, MO). The water was double-distilled and filtered with a laboratory reagent grade water system (Continental Water System Corp., San Antonio, TX).

Phase Diagram. Microemulsion regions were determined in phase diagrams constructed by titrating either the oil phase-surfactant or aqueous phase-surfactant mixtures with the aqueous phase or the oil phase, respectively. The microemulsion region boundaries were determined by visual observation for transparency, and all samples were vigorously stirred, centrifuged, and incubated at 28, 30, and 35 \pm 0.2 °C and were checked for anisotropy under crossed polarized light.

RESULTS AND DISCUSSION

The effect of aqueous phase composition on the size and location of oil-in-water (L_1) and water-in-oil (L_2) microemulsion regions, respectively, at 35 °C is shown in

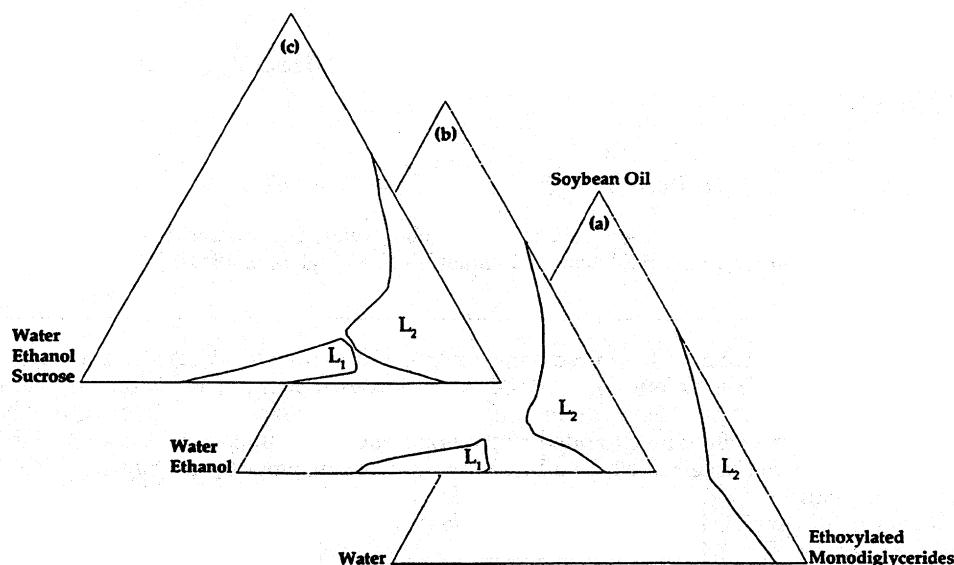


Figure 1. Effect of aqueous phase on oil-in-water (O/W) and water-in-oil (W/O) microemulsion regions (L_1 and L_2), respectively, at 35 °C with aqueous phases: (a) water; (b) 80/20 wt % water/ethanol; (c) 70/20/10 wt % water/ethanol/sucrose.

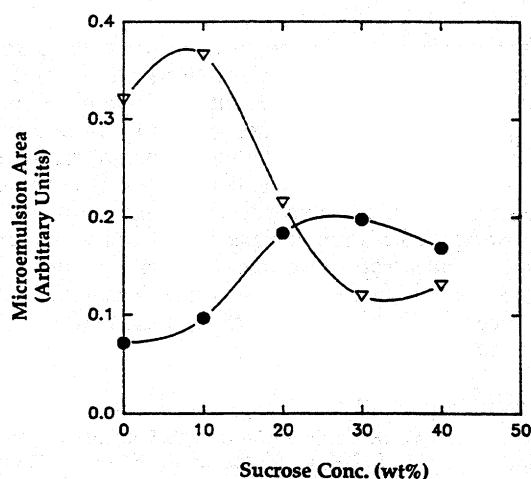


Figure 2. Effect of sucrose concentration on the area of the microemulsion regions for a system containing soybean oil, ethoxylated monodiglyceride/monoglyceride (75/25 wt %), and aqueous phase containing 20 wt % ethanol solution and various amounts of sucrose: (●) L_1 ; (▼) L_2 .

a phase diagram for systems containing soybean oil, ethoxylated monodiglycerides, and different aqueous phases (Figure 1). In Figure 1a, an L_2 phase exists, which on addition of 20 wt % ethanol to the system (Figure 1b), results in the formation of an L_1 phase and an increase in the L_2 phase. Addition of 10 wt % sucrose and 20 wt % ethanol increased both areas (Figure 1c). Ethanol and sucrose act synergistically since addition of 10 wt % sucrose alone to the aqueous phase did not significantly affect the microemulsion regions (Joubran et al., 1993b). Changing surfactant mixtures altered apparent hydrophobicity and had a significant effect on the formation of the isotropic solutions. Fontell et al. (1983) have reported that transition from liquid crystalline mesophases to isotropic solutions is obtained by changes in temperature and composition. Addition of various amounts of sucrose to systems containing soybean oil, ethoxylated monodiglycerides, and 20 wt % ethanol solution showed that sucrose not only enhanced the solubilization of the oil but favored formation of the L_1 phase rather than the L_2 phase (Figure 2). The size and location of the L_1 phase were a function not only of the sucrose content but also of the composition (Fontell et al., 1983) and surfactant mixtures (Shinoda

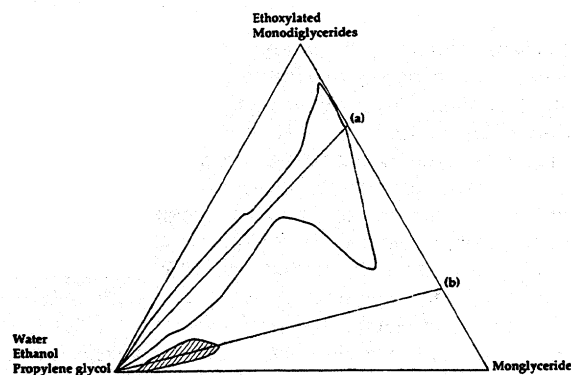


Figure 3. Isotropic and blue-phase (shaded area) regions in phase diagram of ethoxylated monodiglycerides, monoglyceride, and aqueous phase of 70/25/5 wt % water/ethanol/propylene glycol at 30 °C with lines having ethoxylated monodiglyceride/monoglyceride ratios of (a) 75/25 and (b) 25/75 wt %.

and Friberg, 1975). Therefore, monoglycerides were mixed with the ethoxylated monodiglycerides to change the size and location of the L_1 phase.

The isotropic regions of ethoxylated monodiglycerides, monoglyceride, and aqueous phase containing ethanol and propylene glycol are shown in Figure 3. A large isotropic region exists continuously from the surfactant ratio line (a) to the aqueous corner. Another phase, a "blue phase", which under polarized light shows birefringence, existed in the presence of lower ethoxylated monodiglyceride content. This phase consists of droplets whose particle sizes range between those found in microemulsions and those found in emulsions and which are separated by layers of lamellar liquid crystals and appear blue. The existence of this phase appears to be a very stable dispersion and has been reported in the literature. Tiddy (1972) has suggested that it is an emulsion of the lamellar phase in solution. Friberg et al. (1969) have shown that the presence of the liquid crystalline phase enhances the stability of an emulsion and that the blue phase represents a specific case of such a phase. He has also reported the existence of blue phase in systems containing 50 wt % sorbitol solution, sodium dodecyl sulfate, and hexanol (Friberg et al., 1990). Electron micrographs of these systems indicated the presence of a variety of droplet sizes and shapes with lamellar layered structures.

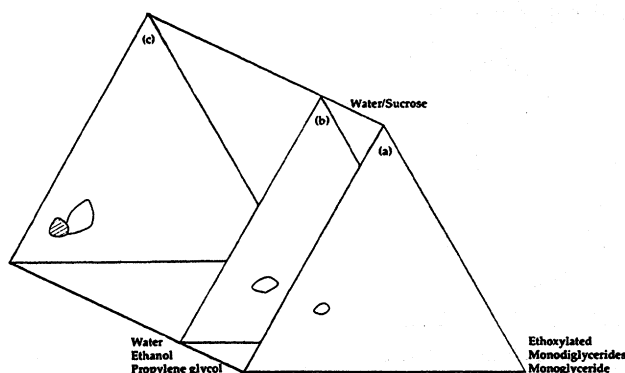


Figure 4. Effect of temperature on isotropic and blue-phase (shaded area) regions in phase diagram containing 25/75 wt % ethoxylated monodiglycerides/monoglyceride, 60 wt % sucrose solution, and aqueous phase of 70/25/5 wt % water/ethanol/propylene glycol at (a) 28, (b) 30, and (c) 35 °C.

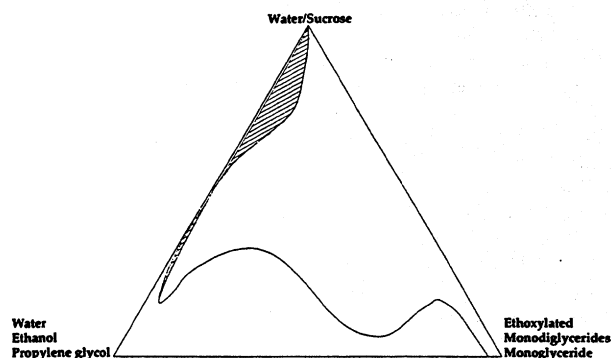


Figure 5. Isotropic and blue phase (shaded area) regions in phase diagram of 75/25 wt % ethoxylated monodiglycerides/monoglyceride, 60 wt % sucrose solution, and 70/25/5 wt % water/ethanol/propylene glycol at 30 °C.

It is clear from Figure 3 that high concentrations of ethoxylated monodiglycerides are needed to form a large isotropic area. Therefore, the phase behavior of systems containing 60 wt % sucrose was investigated at two different ratios of ethoxylated monodiglycerides/monoglyceride to reduce the amount of surfactant required for isotropic solution formation. Figure 4 shows the isotropic

and blue phases at 28, 30, and 35 °C for a system containing a 25/75 wt % ratio of ethoxylated monodiglycerides/monoglyceride. It is seen that the isotropic solutions occupied only a small area and the blue phase appeared only at 35 °C. We have found that these small regions diminish with addition of small amounts of soybean oil and exhibit little utility for oil solubilization. However, isotropic solutions and blue phase are present at low surfactant concentrations in systems containing 75/25 wt % ethoxylated monodiglycerides/monoglyceride, sucrose solution, and aqueous phase (Figure 5). As shown in Figure 5, the blue phase exists at very low surfactant and high sucrose concentrations. The blue phase, however, does not exist in the absence of surfactant. The gradual transition from the blue phase to the isotropic area is due to the addition of alcohol. These isotropic solutions are continuous over a larger area with two maxima at total surfactant/aqueous phase ratios of 90/10 and 30/70 wt %. Addition of soybean oil to this system causes the O/W micellar solution L_1 , at a ratio of 30/70, to shrink, while at a ratio of 90/10 the W/O micellar solution L_2 and the blue phase disappeared (compare Figures 6a and 5). Both W/O and O/W microemulsions exist in a system for which the sucrose solution was replaced with soybean oil (Figure 6b). The sucrose solution apparently promotes triglyceride solubilization in the aqueous phase to form O/W microemulsions but destabilizes the L_2 , W/O microemulsion phase (compare parts a and b of Figure 6). Replacing soybean oil with partially hydrogenated soybean oil resulted in a reduction in the microemulsion area L_1 , indicating that saturated oils are poorly solubilized (Figure 6b,c). No microemulsion region was detected with fully hydrogenated soybean oil.

To improve triglyceride solubility, a short-chain fatty acid triglyceride was used. Figure 7a shows the isotropic solution behavior of coconut oil, indicating that the microemulsion area was slightly bigger at lower surfactant concentrations than that with soybean oil (compare Figures 6a and 7a). In quantitative terms 30 wt % of the coconut oil was solubilized using 4 wt % surfactant; however, 12 wt % of surfactant was required to solubilize the same amount of soybean oil, indicating that short-chain fatty acid triglycerides are more easily solubilized. A blue phase

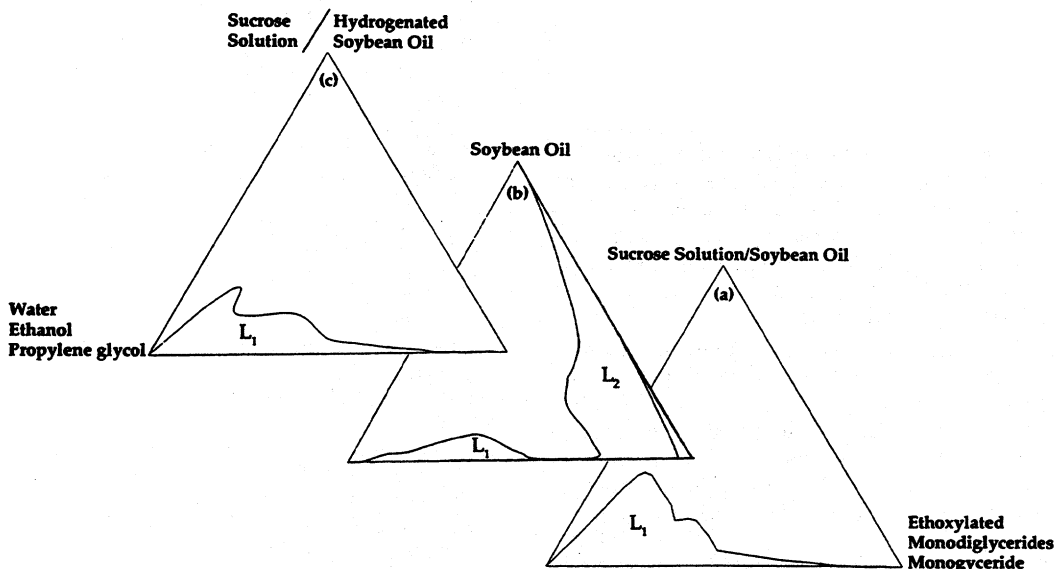


Figure 6. Effect of soybean oil on isotropic microemulsion regions L_1 and L_2 at 30 °C for phase diagram containing 75/25 wt % ethoxylated monodiglycerides/monoglyceride, 70/25/5 wt % water/ethanol/propylene glycol, and (a) 90/10 wt % mixture of 60 wt % sucrose solution/soybean oil, (b) same as (a) without sucrose solution, or (c) same as (a) but replacing soybean oil with partially hydrogenated soybean oil.

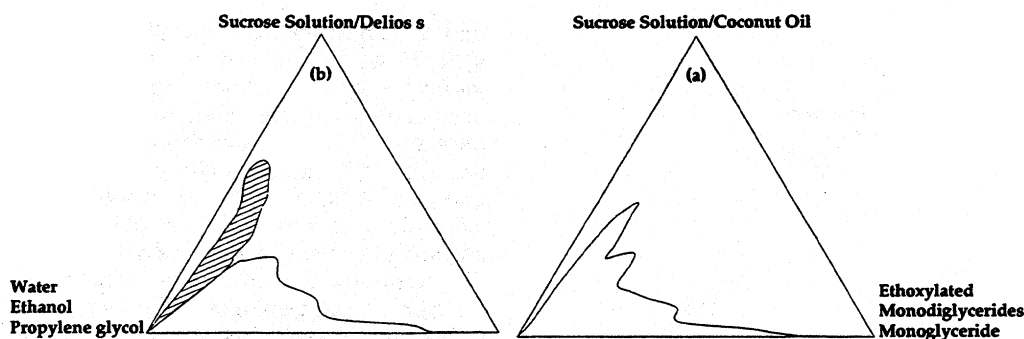


Figure 7. Effect of triglyceride fatty acid chain on isotropic solution and blue phase (shaded area) in phase diagram containing 75/25 wt % ethoxylated monodiglycerides/monoglyceride, 70/25/5 wt % water/ethanol/propylene glycol at 30 °C: (a) 90/10 wt % mixture of 60 wt % sucrose solution/coconut oil; (b) same as (a) with fractionated coconut oil (Delios S).

formed next to the isotropic region for a sucrose solution containing 10 wt % fractionated coconut oil and 75 and 25 wt % of caprylic and capric fatty acids, respectively (Figure 7b).

From a thermodynamic standpoint it has been shown that sucrose can stabilize bilayer systems by modification of forces as demonstrated by LeNeveu et al. (1976). Bilayer separation was correlated with predicted changes of van der Waals forces between lipid bilayers with increasing sugar concentrations. Conversely, micellization of lamellar or hexagonal phases was shown to occur in the presence of strongly chaotropic reagents (e.g., trichloro- and tribromoacetates) by Oku and MacDonald (1983). We have shown that ethanol, when used as a cosolvent, exhibited properties of a chaotropic reagent capable of destroying liquid crystalline mesophases (Joubran et al., 1994). The driving force in retaining triglycerides in aqueous solutions probably occurs through complex formation and the existence of strong hydrogen bonding at the interface. Strong microemulsion interfaces were obtained by stabilizing liquid crystalline phases with sucrose and then destabilizing the system with short-chain alcohols. The fact that the blue phase exists at lower surfactant concentration, and is reasonably stable due to the formation of a liquid crystalline phase, reemphasizes the necessity of having a strong barrier against coalescence. Blum et al. (1985) have suggested that the molecular size of the lipophilic molecules is the most decisive factor in determining the solubility and phase behavior of triglycerides. Alandar et al. (1989b) have compared the behavior and structure of triglyceride microemulsions to those of ordinary hydrocarbons. According to their results, the molecular size of the triglyceride components of the oil was the driving force for better solubilization; e.g., peanut oil, which contains triglycerides that are larger than tricaprylin, was less soluble. This concept could be used to explain our results since the regions of microemulsions prepared with coconut oil were larger than regions prepared with soybean oil. Various degrees of fatty acid unsaturation also affected phase behavior.

The systems studied in this paper were constructed from food grade components. From an industrial point of view, both the microemulsion areas and the blue phase could be attractive systems for making stable products with low fat content, since the latter contains as little as 2.5 wt % surfactant with significant stability as has been pointed out by Friberg et al. (1990). Such microemulsion systems are cost effective since they require only 10 wt % surfactant and, under the proper conditions, are indefinitely stable. The question of converting the blue phase into microemulsions still remains unanswered and will be the subject of a future study.

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